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NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

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DESCRIPTION

Technical Field

This invention relates to a new class of superconducting compositions having high superconducting transition temperatures and methods for using and preparing these compositions, and more particularly to superconducting compositions including copper and/or other transition metals, the compositions being characterized by a superconducting phase and a layer-like structure.

Background Art

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials, including about a quarter of the elements of the periodic table and over 1000 alloys and other multi-component systems. Generally, superconductivity

is considered to be a property of the metallic state of a material since all known superconductors are metallic under the conditions that cause them to be superconducting. A few normally non-metallic materials, for example, become superconducting under very high pressure wherein the pressure converts them to metals before they exhibit superconducting behavior.

Superconductors are known to be very attractive for the generation and energy-saving transport of electrical power over long distances, and as materials used to form the coils of very strong magnets. These magnets are used in, for example, plasma and nuclear physics, nuclear magnetic resonance medical diagnosis systems, and in connection with the magnetic levitation of fast trains.

Other potential uses of superconducting materials occur in power generation systems using thermonuclear fusion where very large magnetic fields must be provided, superconducting magnets being the only possible means for providing such high fields. In addition to these applications, superconductors are known in high speed switching devices, such as Josephson type switches, and in high density packaging and circuit layouts. Superconductors also are used in different types of elec-

tronic instrumentation, such as magnetic susceptometers
and magnetometers.

While the advantages of superconductors are quite obvious to scientists and engineers, the common disadvantage of all presently known superconductive materials lies in their very low transition temperature. This temperature is often called the critical temperature T_c and is the temperature above which superconductivity will not exist. Usually T_c is on the order of a few degrees Kelvin. The element with the highest T_c is niobium whose T_c is 9.2°K . The composition having the highest previously known T_c is Nb_3Ge which exhibits a T_c of about 23°K at ambient pressure. Transition metal alloy compounds of the A15(Nb_3Sn) and B1(NbN) structure have been shown to have high superconducting transition temperatures.

Among the A15 compounds is the aforementioned composition Nb_3Ge . Some of these compositions are described in J. Muller, Rep. Prog. Phys. 43, 663 (1980), and M. R. Beasley et al, Phys. Today, 37 (10), 60 (1984).

It is known in the art that a small number of oxides will exhibit superconductivity. Reference is made to D.C. Johnston et al, Mat. Res. Bull. 8, 777 (1973), which describes high temperature superconductivity in the Li-

Ti-O system with superconducting onsets as high as 13.7°K. These materials have multiple crystallographic phases including a spinel structure exhibiting the high T_c . Other metallic oxides, such as the perovskite Ba-

5 a Pb-Bi-O system can exhibit superconductivity due to high electron-phonon coupling in a mixed valent compound, as described by G. Binnig et al, Phys. Rev. Lett., 45, 1352 (1980), and A.W. Sleight et al, Solid State Communications, 17, 27 (1975).

10 As is evident from the foregoing, superconductors presently known require liquid helium for cooling and this, in turn, requires an elaborate technology and a considerable investment in cost and energy. Accordingly, it is a primary object of the present invention to provide 15 new compositions which exhibit high T_c and methods for using and producing the same.

20 It is another object of the present invention to provide new superconducting compositions and methods for using and making them where cooling with liquid helium is not required in order to have superconductive properties in the compositions.

It is another object of the present invention to provide novel superconductive materials that are multi-valent oxides including transition metals, the compositions having a perovskite-like structure.

5 It is a further object of the present invention to provide novel superconductive compositions that are oxides including rare earth and/or rare earth-like atoms, together with copper or other transition metals that can exhibit mixed valent behavior.

10 It is a still further object of the present invention to provide novel superconductive compositions exhibiting high T_c , where the compositions are oxides including a phase having a layer-like structure and including copper.

15 It is a still further object of the present invention to provide new superconductive compositions exhibiting high T_c , where the superconductive compositions include layered structures including a rare earth and/or rare earth-like element and a transition metal.

20 It is another object of this invention to provide a new class of superconducting compositions characterized by

a T_c greater than 26 °K, and methods for making and using these compositions.

It is another object of this invention to provide new compositions and methods for using them, where the compositions include a multi-valent oxide of copper and exhibit a T_c greater than 26°K.

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The basis for our invention has been described by us in the following previously published article: J.G.

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Bednorz and K.A. Muller, Zeitschrift fur Physik B -
Condensed Matter, 64, pp. 189-193. (Sept. 1986)

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Another article of interest by us is J.G. Bednorz, K.A. Muller, M. Takashige, Europhysics Letters, 3(3), pp. 379-385 (1987).

Summary of the Invention

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This invention relates to novel compositions exhibiting superconductivity at temperatures higher than those obtained in prior known superconductive materials, and to methods for using and forming these compositions. These compositions can carry supercurrents (i.e., electrical

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currents in a substantially zero resistance state of the
composition) at temperatures ~~at~~ greater than 26°K. In
general, the compositions are characterized as mixed
transition metal oxide systems where the transition
metal oxide can exhibit multivalent behavior. These
compositions have a layer-type crystalline structure,
often perovskite-like, and can contain a rare earth or
rare earth-like element. A rare earth-like element

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(sometimes termed a near rare earth element) is one
whose properties make it essentially a rare earth ele-
ment. An example is a group IIIB element of the periodic
table, such as La. Substitutions can be found in the
rare earth (or rare earth-like) site or in the transi-
tion metal sites of the compositions. For example, the
rare earth site can also include alkaline earth elements
selected from group IIA of the periodic table, or a
combination of rare earth or rare earth-like elements
and alkaline earth elements. Examples of suitable
alkaline earths include Ca, Sr, and Ba. The transition
metal site can include a transition metal exhibiting
mixed valent behavior, and can include more than one
transition metal. A particularly good example of a
suitable transition metal is copper. As will be appar-
ent later, Cu- oxide based systems provide unique and
excellent properties as high T_c superconductors.

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An example of a superconductive composition having high T_c is the composition represented by the formula RE-TM-O, where RE is a rare earth or rare earth-like element, TM is a nonmagnetic transition metal, and O is oxygen. Examples of transition metal elements include Cu, Ni, Cr etc. In particular, transition metals that can exhibit multi-valent states are very suitable. The rare earth elements are typically elements 58-71 of the periodic table, including Ce, Nd, etc. If an alkaline earth element (AE) were also present, the composition would be represented by the general formula RE-AE-TM-O.

The ratio (AE,RE) : TM is generally approximately 1:1, but can vary from this as will be shown by examples where the ratio (AE,RE) : TM is 2:1. Of course, the amount of oxygen present in the final composition will adjust depending upon the processing conditions and will be such that the valence requirements of the system are satisfied.

The methods by which these superconductive compositions can be made can use known principles of ceramic fabrication, including the mixing of powders containing the rare earth or rare earth-like, alkaline earth, and

transition metal elements, coprecipitation of these materials, and heating steps in oxygen or air.

A particularly suitable superconducting material in accordance with this invention is one containing copper as the transition metal. Copper can exist in a Cu²⁺ or Cu³⁺ mixed valence state. The state(s) assumed by copper in the overall composition will depend on the amount of oxygen present and on any substitutions in the crystalline structure. Very high T_c has been found in Cu-oxide systems exhibiting mixed valence states, as indicated by conductivity and other measurements. Copper oxide systems including a rare earth or rare earth-like element, and an alkaline earth element, are unique examples of this general class of superconducting layered copper oxides which exhibit T_c greater than 26°K.

These and other objects, features, and advantages will be apparent from the following more particular description of the preferred embodiments.

Brief Description of the Drawings

FIG. 1 is a schematic illustration of a representative circuit used to measure dc conductivity in the high T_c superconductors of this invention.

5 FIG. 2 is a plot of the temperature dependence and resistivity in the composition $Ba_x La_{5-x} Cu_5 O_5(3-y)$ for samples with $x(Ba)=1$ (upper two curves, left scale) and $x(Ba)=0.75$ (lower curve, right scale). The influence of current density through the composition is also shown.

10 FIG. 3 is a plot of the low temperature dependence of resistivity in the composition $Ba_x La_{5-x} Cu_5 O_5(3-y)$ with $x(Ba)=1$, for different annealing conditions (i.e., temperature and oxygen partial pressure).

15 FIG. 4 is a plot of the low-temperature resistivity of the composition $Ba_x La_{5-x} Cu_5 O_5(3-y)$ with $x(Ba)=0.75$, recorded for different densities of electrical current through the composition.

Description of the Preferred Embodiments

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The superconductive compositions of this invention are transition metal oxides generally having a mixed valence and a layer-like crystalline structure, and exhibit T_c 's higher than those of previously known superconducting materials. These compositions can also include a rare earth site in the layer-like structure where this site can be occupied by rare earth and rare earth-like atoms, and also by alkaline earth substitutions such as Ca, Sr, and Ba. The amount of oxygen present will be such that the valence requirements of the system are satisfied, the amount of oxygen being somewhat a function of the processing steps used to make the the superconductive compositions. Non-stoichiometric amounts of oxygen can be present in these compositions. The valence state of the elements in the oxide will be determined by the final composition in a manner well known to chemists. For example, the transition metal Cu may be present in some compositions in both a Cu^{2+} and a Cu^{3+} state.

An example of a superconductive compound having a layer-type structure in accordance with the present invention is an oxide of the general composition RE_2TMO_4 , where RE stands for the rare earths (lanthanides) or rare earth-like elements and TM stands for a transition metal. In these compounds the RE portion can be par-

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tially substituted by one or more members of the alkaline earth group of elements. In these particular compounds, the oxygen content is at a deficit.

For example, one such compound that meets this general
5 description is lanthanum copper oxide La_2CuO_4 in which the lanthanum - which belongs to the IIIB group of elements - is in part substituted by one member of the neighboring IIA group of elements, viz. by one of the alkaline earth metals (or by a combination of the members of the IIA group), e.g., by barium. Also, the oxygen content of the compound can be incomplete such that the compound will have the general composition
10 $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$, wherein $x \leq 0.3$ and $y < 0.5$.

Another example of a compound meeting this general formula is lanthanum nickel oxide wherein the lanthanum is
15 partially substituted by strontium, yielding the general formula $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4-y}$. Still another example is cerium nickel oxide wherein the cerium is partially substituted by calcium, resulting in $\text{Ce}_{2-x}\text{Ca}_x\text{NiO}_{4-y}$.

20 The following description will mainly refer to barium as a partial replacement for lanthanum in a La_2CuO_4 compound because it is in the Ba-La-Cu-O system that

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many laboratory tests have been conducted. Some compounds of the general Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 667-671. They did not, however, find or try to find superconductivity. These references and their teachings regarding perovskite-like layered oxides of mixed valent transition metals, and their preparation, are herein incorporated by reference.

Experiments conducted in connection with the present invention have revealed that high- T_c superconductivity is present in compounds where the rare earth or rare earth-like element is partially replaced by any one or more of the members of the IIA group of elements, i.e., the alkaline earth metals. Actually, the T_c of $\text{La}_2\text{CuO}_{4-y}$ with the substitution Sr^{2+} is higher and its superconductivity-induced diamagnetism larger than that found with the substitutions Ba^{2+} and Ca^{2+} .

The Ba-La-Cu-O system can exhibit a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller Cu^{3+} and Jahn-Teller Cu^{2+} ions.

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This applies likewise to systems where nickel is used in place of copper, with Ni^{3+} being the Jahn-Teller constituent, and Ni^{2+} being the non-Jahn-Teller constituent. The existence of Jahn-Teller polarons in conducting crystals was postulated theoretically by K.H.

Hoeck, H. Nickisch and H. Thomas in Helv. Phys. Acta 56

a ²³⁷_μ(1983) 257. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at higher critical temperatures.

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Samples in the Ba-La-Cu-O system, when subjected to X-ray analysis, revealed three individual crystallographic phases, viz.

- a first layer-type perovskite-like phase, related to the

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K_2NiF_4 structure, with the general composition
 $La_{2-x}Ba_xCuO_{4-y}$, with
 $x \ll 1$ and $y \geq 0$;

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- a second, non-conducting CuO phase; and
- a third, nearly cubic perovskite phase of the general composition $La_{1-x}Ba_xCuO_{3-y}$ which appears to be independent of the exact starting composition.

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Of these three phases the first one appeared to be responsible for the observed high- T_c superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the Ba²⁺ substitution caused a mixed-valent state of Cu²⁺ and Cu³⁺ to preserve charge neutrality. It is assumed that the oxygen deficiency, y, is the same in the doped and undoped crystallites.

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In this application, the terms transition metal oxide, copper oxide, Cu-oxide, etc. are meant to broadly include the oxides which exhibit superconductivity at temperatures greater than 26°K. Thus, the term copper oxide can mean, among other things, an oxide such as CuO_{4-y} in the mixed oxide composition La_{2-x}Ba_xCuO_{4-y}.

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Both La₂CuO₄ and LaCuO₃ are metallic conductors at high temperatures in the absence of barium. Actually, both are metals like LaNiO₃. Despite their metallic character, the Ba-La-Cu-O type materials are essentially ceramics, as are the other compounds of the RE₂TMO₄ type, and their manufacture generally follows the known principles of ceramic fabrication. The preparation of a superconductive Ba-La-Cu-O compound, for example, in

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accordance with the present invention typically involves
the following manufacturing steps:

- Preparing aqueous solutions of the respective nitrates of barium, lanthanum and copper and coprecipitation thereof in their appropriate ratios,
- adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates.
- decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for one to eight hours.
- pressing the resulting product at a pressure of about 4 kbar to form pellets.
- re-heating the pellets to a temperature between 500 and 900°C for one half hour to three hours for sintering.

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It will be evident to those skilled in the art that if the partial substitution of lanthanum by another alkaline earth element, such as strontium or calcium, is desired, the particular nitrate thereof will have to be used in place of the barium nitrate of the example process described above. Also, if the copper of this example is to be replaced by another transition metal, the nitrate thereof will obviously have to be employed. Other precursors of metal oxides, such as carbonates or hydroxides, can be chosen in accordance with known principles.

Experiments have shown that the partial contents of the individual compounds in the starting composition play an important role in the formation of the phases present in the final product. While, as mentioned above, the final Ba-La-Cu-O system obtained generally contains the said three phases, with the second phase being present only in a very small amount, the partial substitution of lanthanum by strontium or calcium (and perhaps beryllium) will result in only one phase existing in the final $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ or $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$, respectively, provided $x < 0.3$.

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With a ratio of 1:1 for the respective (Ba, La) and Cu contents, it is expected that the three phases will occur in the final product. Setting aside the second phase, i.e. the CuO phase whose amount is negligible, the relative volume amounts of the other two phases are dependent on the barium content in the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ complex. At the 1:1 ratio and with an $x = 0.02$, the onset of a localization transition is observed, i.e., the resistivity increases with decreasing temperature, and there is no superconductivity.

With $x = 0.1$ at the same 1:1 starting ratio, there is a resistivity drop at the very high critical temperature of 35°K .

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With a (Ba, La) versus Cu ratio of 2:1 in the starting composition, the composition of the $\text{La}_2\text{CuO}_4:\text{Ba}$ phase, which appears to be responsible for the superconductivity, is imitated, with the result that now only two phases are present, the CuO phase not existing. With a barium content of $x = 0.15$, the resistivity drop occurs at $T_c = 26^{\circ}\text{K}$.

The method for preparing these Ba-La-Cu-O sample complexes used two heat treatments for the precipitate at

an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at 900°^C for a decomposition and reaction period of 5 hours, and again at 900°^C for a sintering period of one hour. These values apply to a 1:1 ratio composition as well as to a 2:1 ratio composition.

For the 2:1 ratio composition, a somewhat higher temperature is permissible owing to the higher melting point of the composition in the absence of excess copper oxide. However, a one-phase compound was not achieved by a high temperature treatment.

Conductivity Measurements (FIGS. 1-4)

The dc conductivity of representative Ba-La-Cu-O compositions was measured to determine their low temperature behavior and to observe their high T_c . These

5 measurements were performed using the well known four-point probe technique, which is schematically illustrated in FIG. 1. Rectangular shaped samples 10 of

a $Ba_x/La_{5-x}/Cu_{5.5}(3-y)$ were cut from sintered pellets, and provided with gold sputtered electrodes 12A and 12B, about 0.5 microns thick. Indium wires 14A and 14B contact electrodes 12A and 12B, respectively. The sample was contained in a continuous flow cryostat 16 (Leybold-Hereaus) and measurements were made over a

a $\begin{matrix} 300-4.2^{\circ}K \\ \diagdown \\ 300-412^{\circ}K \end{matrix}$

10 temperature range $\begin{matrix} 300-4.2^{\circ}K \\ \diagdown \\ 300-412^{\circ}K \end{matrix}$.

15 Electrodes 12A and 12B are connected in a circuit including a current source 18 and a variable resistor 20.

Indium leads 22A and 22B are pressed into contact with sample 10 and fixed with silver paint 24. Leads 22A, 22B are connected to a voltage reading instrument 26.

20 Since the current and voltage are accurately determined, the resistivity of the sample 10 is then known. In the configuration used for these measurements, a computer was used to provide a computer-controlled fully-

automatic system for temperature variation, data acquisition and processing.

In FIG. 2, the low temperature dependence of resistivity

a (ρ , measured in ohm-cms) in the composition

$Ba_x La_{5-x} Cu_5 O_{5(3-y)}$ is plotted for two different values of x. For the upper two curves, the value of x(Ba) is 1 and the left side vertical scale is used. For the lower curve, the value of x is 0.75, and the resistivity scale on the right hand side of the figure is used. The data is taken for different values of current density:

0.25 A/cm² for the top curve and 0.50 A/cm² for the middle and bottom curves.

For barium-doped samples with x(Ba) < 1.0, for example with x < 0.3, at current densities of 0.5A/cm², a high-temperature metallic behavior with an increase in

resistivity at low temperatures was found as depicted in FIG. 2. At still lower temperatures, a sharp drop in resistivity (> 90%) occurred which for higher current densities became partially suppressed (FIG. 1 upper curves, left scale). This characteristic drop was studied as a function of the annealing conditions, i.e. temperature and oxygen partial pressure as shown in FIG.

3. For samples annealed in air, the transition from

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itinerant to localized behavior , as indicated by the minimum in resistivity in the 80°K range, was not found to be very pronounced. Annealing in a slightly reducing atmosphere, however, led to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards the 30°K region. Curves 4 and 5 (FIG. 3), recorded for samples treated at 900°C, show the occurrence of a shoulder at still lower temperatures, more pronounced in curve 6. At annealing temperatures of 1040°C, the highly conducting phase has almost vanished. Long annealing times and/or high temperatures will generally destroy the superconductivity.

The mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in FIG. 2(right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13°K with an onset around 35°K, as shown in FIG. 4 on an expanded temperature scale. FIG. 4 also shows the influence of the current density, typical for granular

compounds. Current densities of 7.5, 2.5, and 0.5 A/cm²
were passed through the superconducting composition.

When cooling the samples from room temperature, the
resistivity data first show a metal-like decrease. At
5 low temperatures, a change to an increase occurs in the
case of Ca substituted compounds and for the Ba-
substituted samples. This increase is followed by a
resistivity drop, showing the onset of superconductivity
at $22 \pm 2^{\circ}\text{K}$ and $33 \pm 2^{\circ}\text{K}$ for the Ca and Ba compounds,
10 respectively. In the Sr compound, the resistivity re-
mains metallic down to the resistivity drop at $40 \pm 1^{\circ}\text{K}$.
The presence of localization effects, however, depends
strongly on alkaline-earth ion concentration and sample
preparation, that is to say, on annealing conditions and
15 also on the density, which have to be optimized. All
samples with low concentrations of Ca, Sr, and Ba show
a strong tendency to localization before the resistivity
drops occur.

20 Apparently, the onset of the superconductivity, i.e. the
value of the critical temperature T_c , is dependent on,
among other parameters, the oxygen content of the final
compound. It seems that for certain materials, an oxy-
gen deficiency is necessary for the material to have a

high- T_c behavior. In accordance with the present invention, the method described above for making the $\text{La}_2\text{CuO}_4:\text{Ba}$ complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the $\text{La}_2\text{CuO}_4:\text{Ba}$ compound likewise applies to other compounds of the general formula RE_2TMO_4 : AE (where AE is an alkaline earth element), such as, e.g. $\text{Nd}_2\text{NiO}_4:\text{Sr}$.

In the cases where a heat treatment for decomposition and reaction and/or for sintering was performed at a relatively low temperature, i.e., at no more than 950°C , the final product is subjected to an annealing step at about 900°C for about one hour in a reducing atmosphere.

It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the RE_2TMO_4 complex, thus creating a distortion in its crystalline structure. The O_2 partial pressure for annealing in this case may be between 10^{-1} and 10^{-5} bar.

In those cases where a relatively high temperature (i.e., above 950°C) is employed for the heat treatment, it might be advantageous to perform the annealing step

in a slightly oxidizing atmosphere. This would make up
for an assumed exaggerated removal of oxygen atoms from
the system owing to the high temperature and resulting
in a too severe distortion of the system's crystalline
structure.

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Resistivity and susceptibility measurements as a function of temperature of Sr^{2+} and Ca^{2+} -doped $\text{La}_2\text{CuO}_{4-y}$ ceramics show the same general tendency as the Ba^{2+} -doped samples: a drop in resistivity ρ (T), and a crossover to diamagnetism at a slightly lower temperature. The samples containing Sr^{2+} actually yielded a higher onset than those containing Ba^{2+} and Ca^{2+} . Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of Sr^{2+} nearly matches that of La^{3+} , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on Ba^{2+} and Ca^{2+} indicate.

The highest T_c for each of the dopant ions investigated occurred for those concentrations where, at room temperature, the $\text{RE}_{2-x}\text{TM}_x\text{O}_{4-y}$ structure is close to the orthorhombic-tetragonal structural phase transition, which may be related to the substantial electron-phonon

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interaction enhanced by the substitution. The alkaline-earth substitution of the rare earth metal is clearly important, and quite likely creates TM ions with no e_g Jahn-Teller orbitals. Therefore, the absence of these Jahn-Teller orbitals, that is, Jahn-Teller holes near the Fermi energy, probably plays an important role in the T_c enhancement.

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While examples have been given using different transition metal elements in the superconducting compositions, copper oxide compositions having mixed valence appear to be unique and of particular importance, having superconducting properties at temperatures in excess of 26°K. These mixed valent copper compositions can include a rare earth element and/or a rare earth-like element which can be substituted for by an alkaline earth element. The amount of oxygen in these compositions will vary depending upon the mode of preparation and will be such as to meet the valence requirements of the composition. These copper-based compositions have a layer-like structure, often of a perovskite type. For a more detailed description of some of the types of crystallographic structures that may result, reference is made to the aforementioned publication by Michel and

Raveau in Rev. Chim. Min. 21, 407 (1984), and to C.

Michel et al, Mat. Res. Bull., Vol. 20, 667-671 (1985).

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While the invention has been described with respect to particular embodiments thereof, it will be apparent to those of skill in the art that variations can be made therein without departing from the spirit and scope of the present invention. For example, while the range of compositions includes rare earth elements and transition metal elements, the ratios of these elements can be varied because the crystalline structure can accommodate vacancies of these elements and still retain a layer-like structural phase exhibiting superconductivity.

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Further, the stoichiometry or degree of non-stoichiometry of oxygen content (i.e., oxygen deficit or surplus) of these compositions can be varied by using reducing or oxidizing atmospheres during formation of the compounds and by using different doping amounts in the rare earth and transition metal sites of the crystal structure. This type of distortion of the crystal structure and the many forms that it can encompass are readily apparent from reference to the aforementioned Michel and Raveau publications. Thus, the invention broadly relates to mixed (doped) transition metal oxides

having a layer-like structure that exhibit superconducting behavior at temperatures in excess of 26°K. Of these materials, a mixed copper oxide having multivalent states provides high T_c and favorable superconducting properties.

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